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(54) **Process for preparing water soluble copolymers of aliphatic monoethylenically unsaturated dicarboxylic acids and unsaturated monomers.**

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## Description

This invention is concerned with the preparation of copolymers which show superior properties as antiscalants, dispersants and incrustation inhibitors. These copolymers comprise, as copolymerized monomer units, units of aliphatic monoethylenically unsaturated dicarboxylic acids, such as maleic acid, and units of at least one comonomer selected from monoethylenically unsaturated monocarboxylic acids, such as acrylic acid, and monoethylenically unsaturated carboxyl-free monomers, such as alkyl esters of acrylic acid.

Copolymers of monoethylenically unsaturated dicarboxylic acids, monoethylenically unsaturated monocarboxylic acids and monoethylenically unsaturated carboxyl-free monomers are useful as antiscalants, dispersants, incrustation inhibitors in detergents, deflocculants and drilling fluid aids. Several techniques employing aqueous solvent systems have been described heretofore for the preparation of these copolymers, including both batch and continuous processes.

The previous art relating to copolymers of the type involved in the present invention recognized the large differences in the reactivity between dicarboxylic monomers such as maleic acid and monocarboxylic monomers such as acrylic acid. In order to obtain complete or nearly complete polymerization of the maleic acid, batch processes using a maleic acid salt "heel" to which is slowly fed the faster polymerizing acrylic acid monomer were the conventional methods of manufacturing these copolymers (US-A-4,659,793). A more recent continuous process uses a long residence time in a complex series of "cascading" reactors (US-A-4,725,655).

Previously, copolymer solutions produced according to the batch "heel type" processes suffered from high levels of unreacted dicarboxylic acid which decreased the effectiveness of the copolymer in certain applications. This problem was presumably solved in US-A-4,659,793 which describes an aqueous batch process for the preparation of copolymers of monoethylenically unsaturated aliphatic dicarboxylic acids, such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, methylene malonic acid, citraconic acid and their monoalkali metal or monoammonium salts, with  $\alpha$ - $\beta$ -ethylenically unsaturated monomers having carboxyl groups, such as methacrylic acid, or sulfonic groups, such as 2-acrylamido-2-methyl propane sulfonic acid. By using (i) a water-soluble radical generating initiator, such as hydrogen peroxide, in concentrations from 0.5 to 10% by weight of the total monomer concentration, and (ii) from 1 to 250 ppm metal ions, such as ferrous or ferric ions, and by controlling the pH in the range of 2 to 7, this procedure was presumably successful in reducing the residual unpolymerized dicarboxylic acid level to less than 0.5% by weight while maintaining control of the copolymer molecular weight. The concentration of the dicarboxylic acid of 4 to 6 carbon atoms per molecule was from 10 to 70% by weight and the concentration of the ethylenically unsaturated monomers of 3 to 10 carbon atoms per molecule was from 30 to 90% by weight, was based on the total weight of the monomers.

In a typical batch procedure described in US-A-4,659,793, a reactor was charged with the dicarboxylic acid along with the metal ion salt. The reaction mixture was heated to a temperature of from 40 to 150 °C and the initiator and the  $\alpha$ , $\beta$ -ethylenically unsaturated monomer in an aqueous solution were then added to the heated reaction mixture over a period of 3 to 10 hours. However, because the reaction process begins with the monoethylenically unsaturated dicarboxylic acid already in the reaction vessel and where the monocarboxylic acid is added along with the initiator over a designated time interval, copolymers with compositions that are changing throughout the reaction are synthesized. During the first stages of the reaction the dicarboxylic acid is present in a high concentration leading to the production of a copolymer composed primarily from the dicarboxylic acid. As the monomer content of the reaction solution changes, increasing in concentration of the added monomer, the composition of the initially manufactured polymer changes, increasing in concentration of the added monomer. Similarly, in the final stages of the reaction, since most of the dicarboxylic acid has been polymerized and the added monomer is now present in a higher concentration relative to the dicarboxylic acid, the composition of the copolymer formed at that stage is primarily made up from the added monocarboxylic monomer.

Another disadvantage of the heel method discussed in US-A-4,659,793 is that, to achieve the more desirable low molecular weight copolymers, a higher level of metal ion is needed during the reaction. However, this is ecologically undesirable since the metal remains in the final product and may eventually find its way into the environment.

Another process for the synthesis of these polymers is a continuous cascade process, disclosed in US-A-4,725,655, which claims to be faster and more economical than a batch process. Described in this patent is the copolymerization of (a) monoethylenically unsaturated dicarboxylic acids, containing from 4 to 6 carbon atoms per molecule, in concentrations of from 10 to 60% by weight of the monomers, (b) monoethylenically unsaturated monocarboxylic acids, containing from 3 to 10 carbon atoms per molecule,

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in concentrations of 40 to 90% by weight of the monomers, and, optionally, carboxyl-free monomers in concentrations of not more than 20% by weight of the monomers. This process, which can only be run continuously, begins by charging all the reaction vessels, typically three, with an aqueous solution of a copolymer of monoethylenically unsaturated mono- and dicarboxylic acids prepared by a batch process according to DE-A-3,147,489. Starting copolymers of similar composition to those being synthesized are used. The reactors are then heated to a temperature of from 60 to 150 °C and the dicarboxylic acid and at least 40% by weight of the monocarboxylic acid are introduced into the first reactor along with from 0.5 to 6.0% by weight of initiator and enough neutralizing solution to neutralize from 20 to 80% by weight of the acids. Additional amounts of monocarboxylic acid and initiator are added to the second reactor or distributed between all the downstream reactors. If a comonomer of a carboxyl-free monomer is used, it can be fed into the first reactor or a combination of the first reactor and the downstream reactors. The total amount of monomer used is from 20 to 70% by weight of the total weight of the aqueous solution. The reaction solution is removed from the last reactor after a residence time of from 0.5 to 8 hours.

Similar to the batch process described above, this continuous process also leads to a polymer with a mixed composition. This is partly due to the fact that the initial charge copolymer was synthesized using a batch process, producing copolymers with skewed (i.e. mixed) compositions. Also, even though all the monomers can be added simultaneously to the first reactor leading to a more consistent composition, once the copolymer enters the second reactor and only monocarboxylic acid and/or carboxyl-free monomers are being added into this reactor, the composition changes and is composed primarily from the added monomers. The multiple reactors and the equipment required for this process, together with the control problems associated with the process, are thought to be disadvantageous in regard to the efficiency of the process and the consistency of the copolymer composition.

We have now found a process, for example, an aqueous batch or continuous process, which enables the preparation, at high conversion, of copolymers of consistent and relatively uniform composition of (i) aliphatic monoethylenically unsaturated dicarboxylic acids, especially maleic acid, with (ii) unsaturated monomers having monocarboxylic acid functionality, such as acrylic acid and/or unsaturated monomers having carboxyl-free functionality such as alkyl esters of acrylic acid. The process involves preparing water-soluble copolymers, which comprises establishing an initial reactor charge of water, gradually adding thereto, under substantially uniform addition rates, monomers, polymerization initiators and neutralizer, as separate streams or mixtures thereof, said monomers, initiators and neutralizer are being cofed and said monomers comprising of from 3 to 65% by weight, for example 5 to 65% by weight based on the total amount of the monomers of at least one monoethylenically unsaturated dicarboxylic acid containing from 4 to 6 carbon atoms per monomer molecule, their salts and the anhydrides of such dicarboxylic acids, and from 35 to 97% by weight, for example 35 to 95% by weight based on the total amount of the monomers of at least one comonomer selected from monoethylenically unsaturated monocarboxylic acids containing from 3 to 6 carbon atoms per monomer molecule and unsaturated noncarboxylic acids, and conducting said reaction in the presence of a metal salt activator at from about 80 to 200 °C, and once said polymerization is complete recovering said copolymer.

According to the present invention there is provided a process for preparing water-soluble copolymers, which comprises:

- (a) establishing an initial charge of water in a reactor;
- (b) gradually adding thereto, monomers, polymerization initiator and neutralizer, which are added as separate streams, or mixtures thereof, with each stream being added at a substantially uniform addition rate and the streams being at least initially cofed with the period of cofed being at least 25%, for example one third or more, of the total period of addition of the streams, and wherein the monomers comprise (A) from 3 to 65% by weight, for example 5 to 65% by weight, based on the total weight of the monomers, of at least one monoethylenically unsaturated dicarboxylic acid containing from 4 to 6 carbon atoms per monomer molecule, or salt or anhydride thereof, and (B) from 35 to 97% by weight, for example 35 to 95% by weight, based on the total weight of the monomers, of at least one comonomer selected from monoethylenically unsaturated monocarboxylic acids containing from 3 to 6 carbon atoms per monomer molecule and unsaturated carboxyl-free monomers;
- (c) adding a metal salt activator to the reactor wherein the metal salt activator can be contained in the initial water charge, added during the addition of the monomers, added after the addition of one or more of the monomers, or a combination thereof;
- (d) running the reaction at a temperature of from about 80 to 200 °C; and
- (e) recovering the resulting copolymer from the reactor.

This relatively uncomplicated process leads to copolymers with a more consistent composition as compared to copolymers made from the prior art processes using the same monomers and may lead to

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copolymers with enhanced properties. Also, the molecular weight of the copolymers can be controlled while both the level of residual monomer and the amount of metal remaining in the final product can be kept at an ecologically acceptable level.

In one embodiment of the process of the invention, to a reactor charged with water and in the presence of a metal salt activator, is gradually added at substantially uniform rates, preferably linearly and separately, three feeds, which may be in the form of solutions, one feed containing the monomers, one feed containing polymerization initiator, and one feed containing neutralizer. An alternate variation involves combining two or more of the three feeds prior to addition to the reactor, and a further alternative involves the addition of the monomers as separate feeds, e.g. solutions.

Copolymers of (i) monoethylenically unsaturated dicarboxylic acids, and (ii) monoethylenically unsaturated monocarboxylic acids and/or monoethylenically unsaturated carboxyl-free monomers, having a weight average molecular weight from about 1000 to 100,000 can be formed by the addition, at substantially uniform addition rates, at least initially, of these monomers along with water-soluble, free radical forming initiators into a reaction vessel.

In the process of the invention, the reactor is initially charged only with water or an aqueous solution of a metal salt activator, and is heated to an increased temperature.

Monomers, initiator and neutralizer are then added, each at a substantially uniform rate. For example, these materials may be added as a simultaneous, linear addition of the cofed materials or as the addition of the cofed materials at slightly different rates and times.

The metal salt activator can be contained in the initial charge, simultaneously cofed into the reaction vessel together with the monomers, added after the addition of one or more of the monomers, or a combination thereof.

The monomers, initiator and neutralizer may be cofed into the reaction vessel, as separate streams, e.g. solutions. Alternatively, two or more of the three streams may be combined, prior to addition to the reactor for example as a single aqueous solution. A further, preferred alternative involves the addition of the monomers as separate streams. The rate and time of addition of the monomers and initiator can be varied to account for the differences in reactivity of the monomers and thereby maximize the conversion of the monomers. This process can be run either as a batch or as a continuous process, the continuous process being preferred.

The ratio of monomers added to the reaction flask corresponds to the ratio contained in the final copolymer product. When the monomers are added as separate cofeeds, they are added at a substantially uniform addition rate, preferably linearly.

Generally, if the monomers are added as separate cofeeds and the monomers used have the same rate of reactivity, it is desirable to start the addition of each of the monomers at about the same time and finish the addition of each of the monomers at about the same time. However, when the reactivity of the monomers differs, the rate of addition may be varied to compensate for this difference in reactivity. When monomers of different reactivity are used, the addition of each of the monomers, or monomer solutions can be started at the same time, but it is desirable to add slower reacting monomers over a shorter period of time as compared to the time of addition of faster reacting monomers. Therefore, the addition of slower reacting monomers will be completed before the addition of faster reacting monomers. Although it is dependent on the rate of reactivity of the monomers, it is more preferred to add slower reacting monomers to the reaction flask in from about 25% to 75% of the time that faster reacting monomers are added. Accordingly, when the monomers are added as separate streams, the addition is such that they are at least initially cofed and the period of such cofeed is at least 25%, and preferably at least 75%, of the total period of monomer addition. Preferably the majority of the monomers, or monomer solutions, are added simultaneously and linearly.

Simultaneous addition of monomers (or alternatively "cofeed") is often followed by a "chase" or finishing polymerization step to reduce unpolymerized, slower reacting monomer by means well known to the polymerization art, such as (a) post-addition of the faster reacting monomers, (b) elevating the polymerization temperature, (c) post-addition of an initiator (catalyst) or combination of these or other techniques.

The monomers, used in the process of the present invention, include monoethylenically unsaturated dicarboxylic acids containing from 4 to 6 carbon atoms per molecule, their salts, e.g. their alkali metal and ammonium salts, and the anhydrides of the cis dicarboxylic acids. Examples of suitable monomers include maleic acid, itaconic acid, mesaconic acid, fumaric add, citraconic acid and the anhydrides of cis dicarboxylic acids, such as maleic anhydride. Maleic anhydride is the most preferable of these monomers. The monoethylenically unsaturated dicarboxylic acid concentration is from 3 to 65% by weight, for example 5 to 65% by weight, and preferably from 10 to 60%, by weight of the total monomer concentration.

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The monomers, used in the process of the invention, also include monoethylenically unsaturated monocarboxylic acids containing from 3 to 6 carbon atoms per molecule, and/or unsaturated carboxyl-free monomers (ie. unsaturated monomers free of carboxyl groups). The concentration of these monomers is from 35 to 97% by weight, for example 35 to 95% by weight, and preferably from 40 to 90%, by weight of the total monomer concentration. Examples of suitable monoethylenically unsaturated monocarboxylic acids include acrylic acid, methacrylic acid, vinyl acetic acid, crotonic acid and acryloxypropionic acid. The most preferred monoethylenically unsaturated monocarboxylic acid is acrylic acid.

Examples of suitable unsaturated carboxyl-free monomers include alkyl esters of acrylic or methacrylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; hydroxyalkyl esters of acrylic or methacrylic acids such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate; acrylamide; methacrylamide; N-tertiary butyl acrylamide; N-methyl acrylamide; N,N-dimethyl acrylamide; acrylonitrile; methacrylonitrile; allyl alcohol; allyl sulfonic acid; allyl phosphonic acid; vinylphosphonic acid; dimethylaminoethyl acrylate; dimethylaminoethyl methacrylate; phosphoethyl methacrylate; N-vinyl pyrrolidone; N-vinylformamide; N-vinylimidazole; ethylene glycol diacrylate; trimethylolpropane triacrylate; diallyl phthalate; vinyl acetate; styrene; vinyl sulfonic acid and its salts; and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and its salts. The concentration of carboxyl-free monomer may be up to about 80% by weight of the total monomer concentration. The concentration is typically up to 35% by weight, and is dependent upon the solubility of the particular monomer in the reaction mixture.

Water-soluble initiators which may be used include hydrogen peroxide, t-butyl hydroperoxide, sodium persulfate, potassium persulfate, ammonium persulfate, sodium perphosphate, ammonium perphosphate, potassium perphosphate, 2,2-azobis(cyanovaleric acid) or combinations thereof. It has been found that the advantageous properties of several of the initiators can be taken advantage of by using them in combination. For example, hydrogen peroxide affords good molecular weight control but at some sacrifice to monomer conversion, while sodium persulfate affords high conversion of monomer to polymer but at some sacrifice to molecular weight control. By combining initiators such as hydrogen peroxide and sodium persulfate, the desirable properties of molecular weight control and high conversion of monomer to polymer can be achieved. The more preferred initiator system is a combination of hydrogen peroxide and sodium persulfate. The total initiator concentration is from 0.5 to 20% and preferably from 1 to 10% by weight based on the total weight of the monomers.

Metal salt activators that may be used in this copolymerization include water-soluble salts of cobalt, iron, copper, nickel, manganese, zirconium and zinc, or combinations thereof. Exemplary of the metal salts are cupric sulfate pentahydrate, ferrous sulfate heptahydrate, cuprous acetate, ferrous acetate, manganese acetate, cerium (IV) sulfate, calcium acetate, calcium sulfate, calcium nitrate, zinc acetate, zinc chloride, titanium (III) chloride, titanium (IV) chloride, lead (II) acetate, lead (IV) acetate, cupric acetate, ferric acetate hydroxide, ferrous and ferric chloride, ferrous and ferric phosphate, cuprous and cupric chloride, cuprous and cupric bromide, cupric nitrate, ferric sulfate, manganese bromide, manganese chloride, cobalt (II) acetate, cobalt (II) chloride, cobalt (II) nitrate, cobalt (II) sulfate, cerium (III) chloride, cerium (III) nitrate, cerium (III) sulfate, zinc nitrate, zinc phosphate, zinc sulfate, manganese nitrate, manganese sulfate, lead (II) chloride, lead (II) nitrate, and the like. The more preferred metal salt activators are the copper containing compounds. It has been found that copper is unique in its ability to control molecular weight and the degree of branching, while maintaining a high conversion of monomer to polymer. This is discussed further in copending U.S. Patent Application Serial No. 475,580, filed on February 6, 1990, and commonly assigned to the same assignee as the present invention. The preferred concentration of the salts are from 1 to 200 ppm, preferably from 1 to 25 ppm, based on the total weight of the monomers.

The metal salt activator helps to control the molecular weight of the polymers. Generally, the higher the metal salt activator concentration, the lower the molecular weight. The lower molecular weight copolymers are the more desirable. However, since the metal salt activator remains in the copolymer during use, and due to current ecological concerns, it is most desirable to limit the amount of metal present in the reaction and therefore limit the amount that ultimately gets into the environment. Therefore, through the optimization of the reaction conditions and the use of, although not limited to, a combination of initiators, the more desirable low molecular weight copolymers can be formed at high conversion using low levels of metal initiator. Even though the metal salt activator can be contained in the initial reactor charge, simultaneously cofed into the reactor vessel together with the monomers, or added after the addition of one or more of the monomers, the more preferred time for the addition of the metal salt activator is after the dicarboxylic acid has been added, and the more preferred addition technique is to add the metal activator (in an aqueous solution) all at one time.

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The polymerization is preferably run to about 20 to 80% by weight solids and most preferably to about 30 to 65% by weight solids. Polymerization temperatures are preferably from 80 to 150 °C, more preferably from 90 to 120 °C. When run in the batch mode, monomer addition times may be from 1 to 10 hours, preferably from 1 to 4 hours, and when run as a continuous process, residence times of at least 30 minutes should preferably be used. If residual monomer levels are higher than desired, a post-polymerization addition of initiator, or initiator and a monomer can be used.

The in-process neutralization by the addition of the neutralizer, e.g. by the addition of solution of from 20 to 80 equivalent percent of base, preferably 40 to 60 percent base, based on the add content of the monomer mixture, is preferably achieved by adding the neutralizer to the reactor linearly throughout the polymerization. The pH of the reaction solution is preferably maintained in the range of from 3 to 7, and most preferably from 4 to 6. Suitable bases include, sodium hydroxide, potassium hydroxide and ammonium hydroxide. A preferred alternative to adding the neutralizer as a separate feed is to combine it with the dicarboxylic acid.

An advantage of the process of the invention is that the relative concentration of monomers in the reaction solution is maintained at a constant ratio to each other and therefore the copolymer so formed has a uniform and consistent composition, as demonstrated by sampling the reaction medium at various times during the course of the reaction and monitoring the monomer composition of the reaction vessel by high performance liquid chromatography (HPLC). Similar sampling of reactions run according to previously described "heel" methods show that, in the early stages of the reaction, a polymer with a high composition of the monomer initially charged in the reactor is formed. As the reaction proceeds, the composition of the polymer increases in the content of the monomer being added until the polymer being formed in the final stages of the reaction consists predominantly of the monomer being added. These results can be seen from the accompanying drawing (Figure 1) in which axis X represents the time (hrs), axis Y represents the % of maleic acid, line "A" represents the maleate copolymer produced by the "heel" process, and line "B" represents the maleate copolymer produced by the process of the invention.

The copolymers of this invention can be added to detergent compositions in concentrations of up to 35% by weight, preferably from 0.1 to 20% by weight, and most preferably from 0.5 to 5.0% by weight, to enhance incrustation inhibition. The compositions can include both a synthetic builder and a water-soluble organic detergent compound such as the anionic, nonionic, zwitterionic, and ampholytic detergent compounds. The chemical nature of these detergent compounds is not an essential feature of the present invention since these are well known to those skilled in the detergent art.

Examples of the builder compounds which can be used in the detergent composition of the present invention include the alkali metal salts of carboxymethyloxysuccinic acid and oxydiacetic add, tetrasodium and tetrapotassium pyrophosphate, pentasodium and pentapotassium tripolyphosphates, ether polycarboxylates, citrates, starch or cellulose derived from polycarboxylates, polyacrylic acids and the like. Other materials which may be present in the detergent composition are those conventionally present therein. Typical examples thereof include soil suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, fillers, abrasives, optical brighteners, enzymes, suds boosters, suds dispersants, germicides, anti-tarnishing agents, cationic detergents, softeners, chlorine releasing agents, buffers and the like. The balance of the detergent composition is water.

The detergent composition of the present invention may be in any of the usual physical forms of such compositions, such as powders, beads, flakes, bars, tablets, noodles, liquids, pastes, and the like. The detergent compositions can be prepared and utilized in the conventional manner.

An additional advantage of the polymers of this invention is that they are somewhat biodegradable. A biodegradable synthetic polymeric detergent additive is preferred since the use of nonbiodegradable polymeric additives can lead to environmental problems due to the build-up of polyacids.

The present invention will now be further illustrated by way of the following Examples which are for illustrative purposes only and are not to be construed as imposing any limitation on the scope of the invention. In the Examples, all percentages are by weight unless specified otherwise.

#### EXAMPLE 1

To a three liter, four neck flask equipped with a mechanical stirrer, reflux condenser and addition funnels, were added 350 grams of deionized water and 8 grams of a 0.15% by weight solution of iron sulfate heptahydrate dissolved in deionized water. This solution was heated to 90 ± 3 °C, at which time a monomer solution of 230 grams of deionized water, 325 grams of glacial acrylic acid and 147.8 grams of maleic anhydride, an initiator solution of 75 grams of deionized water, 25 grams of sodium persulfate and 16.7 grams of 30% hydrogen peroxide, and a neutralizing solution of 300 grams of 50% sodium hydroxide,

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50 equivalent percent based on the monomers, were fed into the flask linearly and separately over 2.5 hours while maintaining the temperature at  $90 \pm 3^\circ\text{C}$ . When the addition was complete, the system was cooled to  $70^\circ\text{C}$  over 30 minutes. At  $70^\circ\text{C}$ , the solution pH was adjusted to about 7 with the addition of 280 grams of a 40% solution of NaOH in water.

- 5 The resultant pH 7 polymer solution had a solids content of 39.5% and a Brookfield viscosity of 0.46 Pa S (460 cps.) at  $25^\circ\text{C}$ . Based on gel permeation chromatography (GPC), the weight average molecular weight (Mw) was 11,900 and the number average molecular weight (Mn) was 4,310. Residual maleic add content was 0.5% and residual acrylic acid content was less than 0.01%, the percentages being based on the total theoretical weight of solids. The biodegradation of the resultant polymer was 3.3% based on a  
10 biological oxygen demand (BOD) test conducted for 30 days.

EXAMPLE 2

- The procedure of Example 1 was repeated except that 25 grams of sodium persulfate dissolved in 75  
15 grams of distilled water was added as the initiator solution. The resultant pH 7.1 polymer solution had a solids content of 40.0% and a Brookfield viscosity of 1.7 Pa S (1700 cps.) at  $25^\circ\text{C}$ . Based on GPC, the Mw was 27,500 and the Mn was 5,340. Residual maleic acid content was 0.7% and residual acrylic acid content was less than 0.02%, the percentages being based on the total theoretical weight of solids.

EXAMPLE 3

- The procedure of Example 1 was repeated except that the neutralizing solution contained 572 grams of  
25 50% sodium hydroxide, 95 equivalent percent based on the monomers, and the post-polymerization neutralization was not performed. The resultant pH 7.8 polymer solution had a solids content of 41.0% and a Brookfield viscosity of 0.17 Pa S (170 cps.) at  $25^\circ\text{C}$ . Based on GPC, the Mw was 5,440 and the Mn was 1,930. Residual maleic add content was 4.2% and residual acrylic acid content was less than 0.02%, the percentages being based on the total theoretical weight of solids

EXAMPLE 4 (Comparative)

- 30 The procedure of Example 1 was repeated except that the neutralizing charge solution was not used. The post-polymerization neutralization solution was increased to 560 grams of a 40% solution of sodium hydroxide in water. The resultant pH 7.7 polymer solution had a solids content of 41.5% and a Brookfield viscosity of 0.25 Pa S (250 cps.) at  $25^\circ\text{C}$ . Based on GPC, the Mw was 10,100 and the Mn was 5,900.  
35 Residual maleic acid content was greater than 5% and residual acrylic acid content was 0.3%, the percentages being based on the total theoretical weight of solids.

EXAMPLE 5

- 40 To a three liter, four neck flask equipped with a mechanical stirrer, reflux condenser and addition funnels, were added 350 grams of deionized water and 8 grams of a 0.15% by weight solution of iron sulfate heptahydrate dissolved in deionized water. This solution was heated to  $90 \pm 3^\circ\text{C}$ , at which time a monomer solution of 240 grams of deionized water, 275 grams of glacial acrylic acid, 147.8 grams of maleic anhydride and 50 grams of vinyl acetate, an initiator solution of 75 grams of deionized water, 25 grams of  
45 sodium persulfate and 16.7 grams of 30% hydrogen peroxide, and a neutralizing solution of 273 grams of 50% sodium hydroxide, 50 equivalent percent based on the concentration of acrylic acid and maleic anhydride, were fed into the flask linearly and separately over 2.5 hours, maintaining the temperature at  $90 \pm 3^\circ\text{C}$ . When the addition was complete, the system was cooled to  $70^\circ\text{C}$  over 30 minutes. At  $70^\circ\text{C}$ , the solution pH was adjusted to about 7 with the addition of 230 grams of a 50% solution of NaOH in water.

- 50 The resultant pH 7.4 polymer solution had a solids content of 41.7% and a Brookfield viscosity of 0.89 Pa S (890 cps.) at  $25^\circ\text{C}$ . Based on GPC, the Mw was 15,500 and the Mn was 5,460. Residual maleic acid content was 0.7%, residual acrylic acid content was 0.01% and residual vinyl acetate content was 0.07%, the percentages being based on the total theoretical weight of solids. The biodegradation of the resultant polymer was 9.6% based on a BOD test conducted for 30 days.

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EXAMPLE 6

The procedure of Example 5 was repeated except that 50 grams of 2-hydroxyethyl methacrylate was substituted for the vinyl acetate. The resultant pH 7.2 polymer solution had a solids content of 41.4% and a Brookfield viscosity of 0.93 Pa S (930 cps.) at 25 °C. Based on GPC, the Mw was 18,500 and the Mn was 5,580. Residual maleic acid content was 0.6%, residual acrylic add content was 0.01% and residual hydroxyethyl methacrylate content was less than 0.01%, the percentages being based on the total theoretical weight of solids. The biodegradation of the resultant polymer was 7.0% based on a BOD test conducted for 30 days.

EXAMPLE 7

To a three liter, four neck flask equipped with a mechanical stirrer, reflux condenser and addition funnels, were added 650 grams of deionized water and 16 grams of a 0.15% by weight solution of iron sulfate heptahydrate dissolved in deionized water. This solution was heated to 90 °±3 °C, at which time a monomer solution of 460 grams of deionized water, 650 grams of glacial acrylic acid and 295.6 grams of maleic anhydride, an initiator solution of 150 grams of deionized water, 50 grams of sodium persulfate and 33.4 grams of 30% hydrogen peroxide, and a neutralizing solution of 600 grams of 50% sodium hydroxide, 50 equivalent percent based on the monomers, were fed into the flask linearly and separately over 2.5 hours, maintaining the temperature at 90 °±3 °C. The temperature was held at 90 °C for an additional 30 minutes after which time 29 grams of acrylic acid and 5 grams of sodium persulfate dissolved in 45 grams of deionized water were added linearly and separately over 30 minutes. When the addition was complete, the system was cooled to 70 °C over 30 minutes. At 70 °C, the solution pH was adjusted to about 7 with the addition of 560 grams of a 40% solution of NaOH in water.

The resultant pH 7 polymer solution had a solids content of 40.0% and a Brookfield viscosity of 0.55 Pa S (550 cps.) at 25 °C. Based on GPC, the Mw was 17,600 and the Mn was 5,210. Residual maleic acid content was 0.2% and residual acrylic add content was less than 0.01%, the percentages being based on the total theoretical weight of solids.

EXAMPLE 8

To a one liter, four neck flask equipped with a mechanical stirrer, reflux condenser and addition funnels, were added 240 grams of deionized water and 16 grams of a 0.15% by weight solution of copper sulfate dissolved in deionized water. This solution was heated to reflux, at which time a monomer solution of 200 grams of glacial acrylic acid and 42.2 grams of maleic anhydride, an initiator solution of 83.3 grams of 30% hydrogen peroxide and a neutralizing solution of 145.5 grams of 50% sodium hydroxide, 50 equivalent percent based on the monomers, were fed into the flask linearly and separately over 2 hours, maintaining reflux. Refluxing was continued for an additional 30 minutes after which time the solution pH was adjusted to about 7 with the addition of 120 grams of a 50% solution of NaOH in water.

The resultant pH 7.3 polymer solution had a solids content of 41.3% and a Brookfield viscosity of 0.3 Pa S (300 cps.) at 25 °C. Based on GPC, the Mw was 4,080 and the Mn was 2,620. Residual maleic acid content was 0.4% and residual acrylic add content was less than 0.1%, the percentages being based on the total theoretical weight of solids.

EXAMPLE 9

To a two liter, four neck flask equipped with a mechanical stirrer, reflux condenser and addition funnels, were added 500 grams of deionized water and 4 grams of a 0.15% by weight solution of copper sulfate pentahydrate dissolved in deionized water. This solution was heated to reflux, at which time a monomer solution of 400 grams of glacial acrylic acid and 100 grams of itaconic acid, an initiator solution of 20.8 grams of 30% hydrogen peroxide, and a neutralizing solution of 412 grams of 50% sodium hydroxide, 75 equivalent percent based on the monomers, were fed into the flask linearly and separately over 3 hours, maintaining reflux. When the addition was complete, the system was cooled to 60 °C over 30 minutes. At 60 °C, the solution pH was adjusted to about 7 with the addition of 81 grams of a 50% solution of NaOH in water followed by the addition of 100 grams of water.

The resultant pH 7 polymer solution had a solids content of 42.9% and a Brookfield viscosity of 30.6 Pa S (30,600 cps.) at 25 °C. Based on GPC, the Mw was 59,700 and the Mn was 14,000. Residual itaconic acid content was 0.04% and residual acrylic acid content was 0.64%, the percentages being based on the total



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theoretical weight of solids.

EXAMPLE 10

5 To a two liter, four neck flask equipped with a mechanical stirrer, reflux condenser and addition funnels, were added 480 grams of deionized water and 32 grams of a 0.15% by weight solution of copper sulfate pentahydrate dissolved in deionized water. This solution was heated to reflux, at which time a monomer solution of 400 grams of glacial acrylic acid and 84.4 grams of maleic anhydride, an initiator solution of 166.6 grams of 30% hydrogen peroxide, and a neutralizing solution of 290.8 grams of 50% sodium hydroxide in 20 grams of deionized water, 75 equivalent percent based on the monomers, were fed into the flask linearly and separately over 3 hours, maintaining reflux. When the addition was complete, the system was cooled to 50 °C over 30 minutes. At 50 °C, the solution pH was adjusted to about 7 with the addition of 197.6 grams of a 50% solution of NaOH.

15 The resultant pH 7 polymer solution had a solids content of 40.9% and a Brookfield viscosity of 0.25 Pa S (250 cps.) at 25 °C. Based on GPC, the Mw was 4,080 and the Mn was 2,620. Residual maleic add content was 0.48% and residual acrylic add content was 0.11%, the percentages being based on the total theoretical weight of solids.

EXAMPLE 11

20 To a two liter, four neck flask equipped with a mechanical stirrer, reflux condenser and addition funnels, were added 500 grams of deionized water and 32 grams of a 0.15% by weight solution of copper sulfate pentahydrate dissolved in deionized water. This solution was heated to 90 ° ± 3 °C, at which time a monomer solution of 400 grams of glacial acrylic acid and 100 grams of itaconic acid, an initiator solution of 166.3 grams of 30% hydrogen peroxide, and a neutralizing solution of 412 grams of 50% sodium hydroxide in 100 grams of deionized water, 75 equivalent percent based on the monomers, were fed into the flask linearly and separately over 3 hours while maintaining the temperature at 90 ° ± 3 °C. When the addition was complete, the system was cooled to 60 °C over 30 minutes. At 60 °C, the solution pH was adjusted to about 7 with the addition of 81.2 grams of a 50% solution of NaOH.

30 The resultant pH 7 polymer solution had a solids content of 37.6% and a Brookfield viscosity of 0.1 Pa S (100 cps.) at 25 °C. Based on GPC, the Mw was 2,550 and the Mn was 1,660. Residual itaconic acid content was less than 0.01% and residual acrylic add content was 0.06%, the percentages being based on the total theoretical weight of solids.

35 The results of the following Examples, 12 to 36, are summarized in Tables 1 to 3. The objective of Examples 12 to 36 was to optimize the present invention in an effort to further reduce the amount of metal activator needed to control the molecular weight of the product and to keep the residual monomer level to a minimum.

Examples 12 to 21

40 To a 2000 ml, four necked round bottom flask was added 250 ml deionized (DI) water and 2.6 ml of a 0.5% solution of copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ). The solution was heated to 92 to 96 °C and the following cofeeds were then added uniformly and linearly to the flask while maintaining the reaction temperature at about 92 to 96 °C: a sodium maleate solution containing 327 grams of a 50% sodium hydroxide solution, 181 grams of maleic anhydride and 305 grams DI water; 390 grams glacial acrylic acid; and a catalyst solution containing 6.1 grams of sodium persulfate, 34 grams of 35% hydrogen peroxide and 50 grams of DI water. The cofeed solutions were all started at the same time. The total times for the addition of the cofeed solutions were varied and are shown in Table 1.

45 After the feeds were completed, the temperature was maintained for 1 hour before cooling to about 65 °C to 75 °C. Once cooled, a series of chasers were added consisting of adding 10 grams of sodium metabisulfite in about 30 grams of DI water followed by the addition of 7 grams acrylic acid. Then the following chaser sequence of adding 2 grams of t-butyl hydroperoxide and 2 grams sodium metabisulfite in about 4 grams of water was performed and then repeated two more times. The batch was then cooled to 55 °C and 352 grams of a 50% solution of sodium hydroxide was added with good agitation and cooling.

55 The residual monomer levels were measured and are compiled in Table 1 along with the molecular weights of the copolymers, the residual monomer levels being expressed as percentages by weight, based on the total theoretical weight of solids.

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TABLE 1

Example	Maleate	Addition Times, Min.			Residual, %	
		AA	Catalyst	Mw	AA	Maleic
					(Before / After Chaser)	
12	240	240	240	22,000	1.4/0.1	2.2/0.5
13	240	240	240	38,000	0.7/0.13	2.7/1.0
14	180	180	180	28,000	0.18/0.11	2.1/0.88
15	180	180	180	30,000	0.16/0.10	2.2/0.98
16	150	180	180	20,000	0.18/nil	1.26/0.05
17	150	180	180	22,000	0.1/nil	1.1/0.05
18	120	180	180	25,000	0.06/0.02	0.79/0.17
19	120	180	180	24,000	0.06/0.02	0.72/0.14
20*	90	180	180	16,000	0.30/0.14	0.76/0.37
21*	60	180	180	15,000	0.30/0.08	0.5/0.2

\* The only chaser step used was the addition of 10 grams of sodium metabisulfite in 30 grams of DI water.

## Example 22 to 26

To a 2000 ml, four necked round bottom flask was added 240 ml deionized (DI) water and 2.6 ml of a 0.5% solution of copper nitrate. The solution was heated to 92 to 96 °C and the following cofeeds were added uniformly and linearly to the flask while maintaining the reaction temperature at about 92 to 96 °C: a sodium maleate solution containing 327 grams of a 50% sodium hydroxide solution, 181 grams of maleic anhydride and 305 grams DI water; 376 grams glacial acrylic acid; and a catalyst solution containing sodium persulfate or hydrogen peroxide or both and 40 grams of DI water. The amount of sodium persulfate and hydrogen peroxide contained in the catalyst feed was varied and is shown in Table 2, the amounts being expressed as percentages based on the weight of monomers. All the feeds were started at approximately the same time and the sodium maleate feed was completed in 120 minutes, the acrylic acid feed was completed in 180 minutes and the catalyst feed was completed in 240 minutes.

After the feeds were completed, the temperature was maintained for 1 hour before cooling to about 65 °C to 75 °C. Once cooled, a series of chasers were added consisting of adding 10 grams of sodium metabisulfite in about 30 grams of DI water followed by the addition of 21 grams acrylic acid. Then the following chaser sequence of adding 2 grams of t-butyl hydroperoxide and 2 grams sodium metabisulfite in about 4 grams of water was repeated three times. The batch was then cooled to 55 °C and 352 grams of a 50% solution of sodium hydroxide was added with good agitation and cooling.

The residual monomer levels are compiled in Table 2 and are compared to the experimental variables, the residual monomer levels being expressed as percentages, based on the total theoretical weight of solids.

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TABLE 2

Example	H <sub>2</sub> O <sub>2</sub> , %	NaPS*, %	Mw	Residual, %	
				AA	Maleic
				(Before / After Chaser)	
22	0	4	19,200	0.14/0.10	0.24/0.001
23	0.25	4	15,600	0.25/0.06	2.3/0.56
24	0.50	4	16,300	0.13/0.04	1.9/0.30
25	2	1	22,700	0.11/0.04	0.98/0.09
26	3	0	29,700	0.19/0.22	2.2/1.20

\* NaPS represents sodium persulfate

### Example 27 to 38

To a 2000 ml, four necked round bottom flask was added 250 ml deionized (DI) water and heated to 92 to 96 °C. The following cofeeds were added uniformly and linearly to the flask while maintaining the reaction temperature at about 92 to 96 °C: a sodium maleate solution containing 327 grams of a 50% sodium hydroxide solution, 181 grams of maleic anhydride and 305 grams DI water; 376 grams glacial acrylic acid; and a catalyst solution containing sodium persulfate, hydrogen peroxide and 60 grams DI water. The amount of sodium persulfate and hydrogen peroxide contained in the catalyst feed was varied and is shown in Table 3, the amounts being expressed as percentages based on the weight of monomers. The cofeed solutions were all started at the same time. The total times for the addition of the cofeed solutions were varied and are also shown in Table 3. An additional feed solution containing 0.013 grams of copper nitrate in 2.6 grams of DI water was added as a "single shot" during the reaction. The time of addition of this metal activator solution was varied and is shown in Table 3.

After the feeds were completed, the temperature was maintained for 1 hour before cooling to about 65 °C to 75 °C. Once cooled, chaser sequences were added consisting of adding 30 grams of sodium metabisulfite in about 90 grams of DI water followed by the addition of 21 grams acrylic acid. Then the following chaser sequence of adding 2 grams of t-butyl hydroperoxide and 2 grams sodium metabisulfite in about 4 grams of water was repeated three times. The batch was then cooled to 55 °C and 352 grams of a 50% solution of sodium hydroxide was added with good agitation and cooling.

The residual monomer levels are compiled in Table 3 and are compared to the experimental variables, the residual monomer levels being expressed as percentages, based on the total theoretical weight of solids.

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TABLE 3

Example	Addition Times, Min.			H <sub>2</sub> O <sub>2</sub> %	NaPS**%	Mw	Time of Cu			Residual, %
	Maleate	AA	Catalyst				Min*	Addition		
								AA	Maleic	
								(Before / After Chaser)		
27	120	180	240	0.5	4	16,300	0	0.13/0.04	1.9/0.3	
28	120	180	240	0.5	4	34,500	+90	0.05/nil	0.6/0.004	
29	120	180	240	0.5	4	47,400	+120	0.03/nil	0.26/0.002	
30	120	180	240	0.5	4	54,900	+165	0.13/nil	0.05/0.001	
31	90	180	240	0.5	4	25,100	+90	0.14/0.01	0.26/0.018	
32	90	180	240	0.5	4	39,900	+120	0.01/nil	0.04/0.003	
33	60	180	180	2	1	15,000	0	0.3/0.08	0.5/0.2	
34	60	180	180	2	1	28,500	+100	0.3/---	0.2/---	
35	60	180	180	2	1	28,500	+100	0.04/---	0.12/---	
36	90	180	180	2	1	15,000	0	0.3/0.14	0.8/0.37	
37	90	180	180	2	1	41,000	+100	0.2/---	0.4/---	
38	90	180	180	2	1	32,400	+100	0.04/---	0.22/---	

\*Cu was added as one shot at the specified time after polymerization began. When the time of the addition is 0, Cu was contained in the initial charge.

\*\* NaPS represents sodium persulfate.

#### Example 39

(Determination of Clay Dispersancy)

The polymers of Examples 9, 10, and 11 were examined for their ability to act as a clay dispersant. Table 4 is a compilation of the viscosity data of various clay slurries containing these polymers. The following is the procedure used to generate these data.

The first step in preparing the clay slurry was to prepare a polymer/blend stock solution. This was done by mixing the polymer with soda ash and deionized water to yield 100 grams of solution. Two blends were prepared, one containing 10% polymer and 15% soda ash, and one containing 15% polymer and 10% soda

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ash. A clay slurry was then prepared by adding a portion of the blend to a mixing cup along with deionized water so that the total weight was 210 grams. Enough of the blend was used so that the amount of polymer present in the slurry corresponded to the initial dosage in Table 4. The cup was then placed on a Hamilton Beach multimixer at low speed, and 490 grams of dry clay were added. Once all the clay had been added, the speed was increased to high and the mixture was allowed to stir for an additional 5 minutes. Then 500 grams of the slurry was transferred from the mixing cup to a pint jar and allowed to cool to ambient temperature. The slurry was then mixed for 1 minute at low speed on the multimixer and then the viscosity was measured using a Brookfield model DV-II viscometer at 20 RPM (spindle #2). The reading was taken one minute after starting the viscometer. After the initial reading, more of the blend was added to the slurry to increase the concentration of polymer by 0.0125% (based on the clay solids), followed by the addition of enough clay to keep the slurry at 70% solids. The slurry was again mixed for one minute on the multimixer at low speed and the viscosity measured. This procedure was repeated until two consecutive additions result in an increased viscosity. The optimum dosage is defined as the dosage which gave the lowest viscosity.

TABLE 4

Polymer	Effect of Maleate Polymers as Clay Dispersants					
	Dosage of Polymer vs. Viscosity -Pa S (cps.)					
	0.1625	0.175	0.1875	0.20	0.2125	0.225
Example 9	1.13 (1130)	0.89 (890)	0.73 (730)	0.392 (392)	0.344 (344)	0.246 (246)
Example 10	0.680 (680)	0.320 (320)	0.286 (286)	0.282 (282)	0.296 (296)	0.290 (290)
Example 11	0.845 (845)	0.730 (730)	0.348 (348)	0.328 (328)	0.340 (340)	

EXAMPLE 40(Semi-Continuous Polymerization)

To a two liter, four neck flask equipped with a mechanical stirrer, reflux condenser, addition funnels, and a bottom outlet, was added 200 grams of deionized water. The water was heated to  $96 \pm 3^\circ \text{C}$ , at which time a monomer solution containing 1,275 grams of deionized water, 1,392 grams of glacial acrylic add, 710 grams of maleic anhydride and 9 grams of a 0.5% by weight solution of copper nitrate trihydrate, an initiator solution containing 234 grams of deionized water and 210 grams of 35% hydrogen peroxide, and a neutralizing solution containing 1,284 grams of 50% sodium hydroxide and 360 grams of deionized water, were added to the flask linearly and separately, while maintaining the temperature at  $96 \pm 3^\circ \text{C}$ . After 90 minutes, approximately one third (1/3) of each of these solutions had been added and as they continued to be added, an additional feed containing 400 grams of deionized water was started at a rate of 200 grams of deionized water per 90 minutes. Simultaneously to the start of the addition of the deionized water, the bottom outlet valve was opened and the contents of the reaction flask were drained at a rate which maintained the total weight of the reactor flask at 2,024.7 grams. After a total elapse time of 270 minutes, all the feeds were finished and the remaining 2,024.7 grams of solution in the flask continued to drain at the same rate over 90 minutes while maintaining the temperature at  $96 \pm 3^\circ \text{C}$ . The product from the first kettle was fed into a second kettle where the temperature was maintained at  $96 \pm 3^\circ \text{C}$ . To each 350 grams of product from the first kettle was added 9.7 grams of glacial acrylic acid and 12.2 grams of 35% hydrogen peroxide. After a residence time of at least 90 minutes, the polymer solution was fed into a third kettle and held at  $96 \pm 3^\circ \text{C}$  until the polymerization was complete and only trace amounts of monomer remained. Finally, the solution was cooled to  $70^\circ \text{C}$  over 30 minutes and the pH was adjusted to about 7 by the addition of 280 grams of a 40% solution of NaOH in water.

The resultant pH 7.9 polymer solution had a solids content of 40.8% and a Brookfield viscosity of 1.375 Pa S (1,375 cps.) at  $25^\circ \text{C}$ . Based on GPC, the Mw was 26,900 and the Mn was 6,00. Residual maleic add content was less than 0.05% and residual acrylic add content was less than 0.15%, the percentages being based on the total theoretical weight of solids.

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**EXAMPLE 41 (Comparative-The Heel Process)**

To a two liter, four neck flask equipped with a mechanical stirrer, reflux condenser and addition funnels, were added 148 grams of maleic anhydride, 470 grams of deionized water and 8.3 grams of a 0.15% by weight solution of iron sulfate heptahydrate dissolved in deionized water. To the flask was gradually added 242 grams of 50% sodium hydroxide. The solution was heated to  $90 \pm 3^\circ\text{C}$ , at which time 325 grams of glacial acrylic acid, and an initiator solution of 65 grams of deionized water, 5 grams of sodium persulfate and 45 grams of 30% hydrogen peroxide were fed into the flask linearly and separately over 3 hours while maintaining the temperature at  $90 \pm 3^\circ\text{C}$ . When the addition was complete, the system was cooled to  $70^\circ\text{C}$ , 310 grams of deionized water was added as a dilution, and then the system was cooled to room temperature.

The resultant pH 4 polymer solution had a solids content of 40.0% and a Brookfield viscosity of 1.5 Pa S (1,500 cps.) at  $25^\circ\text{C}$ . Based on GPC, the Mw was 25,000 and the Mn was 8,800. Residual maleic acid content was 0.13% and residual acrylic add content was less than 0.1%, the percentages being based on the total theoretical weight of solids.

**EXAMPLE 42****(Incrustation Inhibition)**

This Example is an illustration of the incrustation inhibiting properties of a detergent containing a copolymer produced according to the present invention and a comparison of said detergents to detergents containing copolymers produced according to the heel process of the prior art. Laundered in a European style home washing machine were 3 kg. of cotton and cotton/polyester fabric which included two terry towels. To the  $90^\circ\text{C}$  wash water which had a hardness of 350 ppm Ca/Mg (3/1) was added 0.8% by weight of a typical European soda ash/Zeolite detergent containing 3% by weight of the copolymer produced according to the present invention. The towels were laundered for the indicated number of cycles (Table 5), ashed at  $800^\circ\text{C}$  for 2 hours and the inorganic content (incrustation) determined.

The results are shown in Table 5.

TABLE 5

Polymer	Effect of Polymer in Residue Reduction	
	% Ash on Fabric	
	10 Wash Cycles	25 Wash Cycles
Example 40 (heel process)	1.1	1.8
Example 39 (continuous)	0.8	1.5
Sokalan CP-5 (trademark of BASF)	1.1	1.8

The compositions of this invention may be useful as detergent additives, antiscalants, deflocculants, dispersants, drilling fluid aids used in oil drilling operations, and especially useful as incrustation inhibitors.

**Claims**

1. A process for preparing water-soluble copolymers, which comprises:

(a) establishing an initial charge of water in a reactor;

(b) gradually adding thereto, monomers, polymerization initiator and neutralizer, which are added as separate streams, or mixtures thereof, with each stream being added at a substantially uniform addition rate and the streams being at least initially cofed with the period of cofeed being at least 25%, for example one third or more, of the total period of addition of the streams, and wherein the monomers comprise (A) from 3 to 65% by weight, for example 5 to 65% by weight based on the total weight of the monomers, of at least one monoethylenically unsaturated dicarboxylic acid containing from 4 to 6 carbon atoms per monomer molecule, or salt or anhydride thereof, and (B) from 35 to 97% by weight, for example 35 to 95% by weight based on the total weight of the monomers, of at least one comonomer selected from monoethylenically unsaturated monocarboxylic acids containing from 3 to 6 carbon atoms per monomer molecule and unsaturated monomers free of carboxyl groups;

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- (c) adding a metal salt activator to the reactor wherein the metal salt activator can be contained in the initial water charge, added during the addition of the monomers, added after the addition of one or more of the monomers, or a combination thereof;
- (d) running the reaction at a temperature of from about 80 to 200 ° C; and
- (e) recovering the resulting copolymer from the reactor.
2. A process as claimed in claim 1 wherein the monomers are added as separate monomer streams and the addition is such that the monomers are at least initially cofed and the period of such cofeed is at least 25% of the total period of monomer addition.
  3. A process as claimed in claim 1 or 2 wherein the metal salt activator is selected from the salts of cobalt, iron, copper, nickel, manganese, zirconium and zinc and is present in an amount of from 1 to 200 ppm, based on the total weight of the monomers.
  4. A process as claimed in any preceding claim wherein the dicarboxylic acid concentration is from 10 to 60% by weight, based on the total weight of the monomers.
  5. A process as claimed in any preceding claim wherein the dicarboxylic acid is selected from maleic acid, itaconic acid, mesaconic acid, fumaric acid, citraconic acid, salts thereof, anhydrides thereof, and combinations thereof.
  6. A process as claimed in any preceding claim wherein the initiator concentration is from 0.5 to 20% by weight, preferably from 1 to 10% by weight, based on the weight of the monomers, and/or wherein the initiator is selected from hydrogen peroxide, t-butyl hydroperoxide, sodium persulfate, potassium persulfate, ammonium persulfate, sodium perphosphate, ammonium perphosphate, potassium perphosphate and 2,2-azobis(cyanovaleric acid).
  7. A process as claimed in any preceding claim wherein a combination of two or more initiators is used.
  8. A process as claimed in any preceding claim wherein the polymerization is run at a solids level in the range of from 20 to 80%, for example in the range of from 30 to 65%, by weight.
  9. A process as claimed in any preceding claim wherein the monocarboxylic monomer is selected from acrylic acid, methacrylic acid, vinyl acetic acid, crotonic acid and acryloxypropionic acid.
  10. A process as claimed in any preceding claim wherein the monomer free of carboxyl groups is selected from: alkyl esters of acrylic and methacrylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; hydroxyalkyl esters of acrylic and methacrylic acids such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate; acrylamide; methacrylamide; N-tertiary butyl acrylamide; N-methyl acrylamide; N,N-dimethyl acrylamide; acrylonitrile; methacrylonitrile; allyl alcohol; allyl sulfonic acid; allyl phosphonic acid; vinylphosphonic acid; dimethylaminoethyl acrylate; dimethylaminoethyl methacrylate; phosphoethyl methacrylate; N-vinyl pyrrolidone; N-vinylformamide; N-vinylimidazole; ethylene glycol diacrylate; trimethylolpropane triacrylate; diallyl phthalate; vinyl acetate; styrene; vinyl sulfonic acid and salts thereof; and 2-acrylamido-2-methyl propane sulfonic acid and salts thereof.
  11. A process as claimed in any preceding claim wherein one or more of the monomers, polymerization initiator and neutralizer streams are in the form of a solution.
  12. A process as claimed in any preceding claim wherein an aqueous solution of a mixture of the dicarboxylic acid, monocarboxylic acid and monomers free of carboxyl groups is added to the reactor.
  13. A process as claimed in any preceding claim wherein the polymerization pH is maintained in the range of 4 to 6 by the addition of from 20 to 80 equivalent percent of base, based on the acid content of the monomers.

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14. A process as claimed in any preceding claim, wherein the monomers have differing reaction rates and the product from step (d) contains residual unreacted slower reacting monomer, and wherein the level of such unreacted slower reacting monomer is reduced by, following step (d), conducting one or more of the following additional steps:-
- 5 (a) addition of further faster reacting monomer;  
(b) addition of further initiator; and  
(c) elevating the polymerization temperature.
15. A process for preparing water-soluble copolymers, which comprises establishing an initial reactor charge of water, gradually adding thereto, under substantially uniform addition rates, monomers, polymerization initiators and neutralizer, as separate streams or mixtures thereof, said monomers, initiators and neutralizer are being cofed and said monomers comprising of from 3 to 65% by weight, for example 5 to 65% by weight based on the total amount of the monomers of at least one monoethylenically unsaturated dicarboxylic acid containing from 4 to 6 carbon atoms per monomer molecule, their salts and the anhydrides of such dicarboxylic acids, and from 35 to 97% by weight, for example 35 to 95% by weight based on the total amount of the monomers of at least one comonomer selected from monoethylenically unsaturated monocarboxylic acids containing from 3 to 6 carbon atoms per monomer molecule and unsaturated monomers free of carboxyl groups, and conducting said reaction in the presence of a metal salt activator at from about 80 to 200 °C, and once said polymerization is complete recovering said copolymer.
16. A detergent composition, which comprises a water-soluble detergent compound selected from anionic, nonionic, zwitterionic, ampholytic detergent compounds, and mixtures thereof; a builder selected from the alkali metal salts of carboxymethyloxysuccinic acid and oxydiacetic acid, tetrasodium and tetrapotassium pyrophosphate, pentasodium and pentapotassium tripolyphosphates, ether polycarboxylates, citrates, starch or cellulose derived from polycarboxylates, and polyacrylic acids, and up to about 35% by weight, for example from 0.1 to 20% by weight, and preferably from 0.5 to 5.0% by weight, of a copolymer prepared according to the process of any of claims 1 to 15.

## 30 Patentansprüche

1. Verfahren zur Herstellung wasserlöslicher Copolymere, umfassend:
- (a) Herstellen eines Anfangseinsatzmaterials von Wasser in einem Reaktor,
- (b) allmähliches Dazugeben von Monomeren, Polymerisationsinitiator und Neutralisationsmittel, die als separate Ströme oder Gemische davon zugegeben werden, wobei jeder Strom bei einer im wesentlichen einheitlichen Zugabegeschwindigkeit zugegeben wird, und die Ströme mindestens anfänglich co-zugeführt werden, wobei die Zeitspanne der Co-Zufuhr mindestens 25 %, beispielsweise ein Drittel oder mehr, der gesamten Zugabezeitspanne der Ströme beträgt, und worin die Monomeren umfassen (A) von 3 bis 65 Gew.-%, beispielsweise 5 bis 65 Gew.-%, basierend auf dem Gesamtgewicht der Monomeren, von mindestens einer monoethylenisch ungesättigten Dicarbonsäure mit von 4 bis 6 Kohlenstoffatomen pro Monomermolekül oder Salze oder Anhydride davon und (B) von 35 bis 97 Gew.-%, beispielsweise 35 bis 95 Gew.-%, basierend auf dem Gesamtgewicht der Monomeren, von mindestens einem Comonomer, ausgewählt aus monoethylenisch ungesättigten Monocarbonsäuren mit von 3 bis 6 Kohlenstoffatomen pro Monomermolekül und ungesättigten Monomeren, die frei von Carboxylgruppen sind,
- (c) Zugeben eines Metallsalzaktivators zu dem Reaktor, wobei der Metallsalzaktivator in dem Anfangseinsatzmaterial von Wasser enthalten sein kann, das während dem Zugeben der Monomeren, nach dem Zugeben eines oder mehrere der Monomeren oder einer Kombination davon zugegeben worden ist,
- (d) Durchführen der Reaktion bei einer Temperatur von etwa 80 bis 200 °C und
- (e) Gewinnen des erhaltenen Copolymers vom Reaktor.
2. Verfahren nach Anspruch 1, worin die Monomeren als getrennte Monomerströme zugegeben werden und die Zugabe derart ist, daß die Monomeren zumindest anfänglich co-zugeführt werden, und die Zeitspanne einer derartigen Co-Zufuhr mindestens 25 % der gesamten Zeitspanne der Monomerzugabe beträgt.



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3. Verfahren nach Anspruch 1 oder 2, worin der Metallsalzaktivator ausgewählt ist aus den Salzen von Kobalt, Eisen, Kupfer, Nickel, Mangan, Zirkonium und Zink und in einer Menge von 1 bis 200 ppm, basierend auf dem Gesamtgewicht der Monomeren, zugegen ist.
- 5 4. Verfahren nach einem der vorhergehenden Ansprüche, worin die Dicarbonsäurekonzentration von 10 bis 60 Gew.-%, basierend auf dem Gesamtgewicht der Monomeren, beträgt.
5. Verfahren nach einem der vorhergehenden Ansprüche, worin die Dicarbonsäure ausgewählt ist aus Maleinsäure, Itaconsäure, Mesaconsäure, Fumarsäure, Citraconsäure, Salze davon, Anhydride davon  
10 und Kombinationen davon.
6. Verfahren nach einem der vorhergehenden Ansprüche, worin die Initiatorkonzentration von 0,5 bis 20 Gew.-%, vorzugsweise von 1 bis 10 Gew.-%, basierend auf dem Gewicht der Monomeren, beträgt, und/oder worin der Initiator ausgewählt ist aus Wasserstoffperoxid, t-Butylhydroperoxid, Natriumpersulfat, Kaliumpersulfat, Ammoniumpersulfat, Natriumperphosphat, Ammoniumperphosphat, Kaliumperphosphat und 2,2-Azobis(cyanovaleriansäure).  
15
7. Verfahren nach einem der vorhergehenden Ansprüche, worin eine Kombination von zwei oder mehr Initiatoren verwendet wird.  
20
8. Verfahren nach einem der vorhergehenden Ansprüche, worin die Polymerisation bei einem Feststoffgehalt im Bereich von 20 bis 80 Gew.-%, beispielsweise im Bereich von 30 bis 65 Gew.-%, durchgeführt wird.
- 25 9. Verfahren nach einem der vorhergehenden Ansprüche, worin das Monocarboxylmonomer ausgewählt ist aus Acrylsäure, Methacrylsäure, Vinylessigsäure, Crotonsäure und Acryloxypropionsäure.
10. Verfahren nach einem der vorhergehenden Ansprüche, worin das Monomer, das frei von Carboxylgruppen ist, ausgewählt ist aus: Alkylestern von Acryl- und Methacrylsäuren, wie Methylacrylat, Ethylacrylat, Butylacrylat, Methylmethacrylat, Ethylmethacrylat, Butylmethacrylat und Isobutylmethacrylat; Hydroxyalkylestern von Acryl- und Methacrylsäuren, wie Hydroxyethylacrylat, Hydroxypropylacrylat, Hydroxyethylmethacrylat und Hydroxypropylmethacrylat; Acrylamid; Methacrylamid; N-tertiäres-Butylacrylamid; N-Methylacrylamid; N,N-Dimethylacrylamid; Acrylonitril; Methacrylonitril; Allylalkohol; Allylsulfonsäure; Allylphosphonsäure; Vinylphosphonsäure, Dimethylaminoethylacrylat; Dimethylaminoethylmethacrylat; Phosphoethylmethacrylat; N-Vinylpyrrolidon; N-Vinylformamid; N-Vinylimidazol; Ethylenglykoldiacrylat; Trimethylolpropantriacyrlat; Diallylphthalat; Vinylacetat; Styrol; Vinylsulfonsäure und Salzen davon; und 2-Acrylamido-2-methylpropansulfonsäure und Salzen davon.  
30
11. Verfahren nach einem der vorhergehenden Ansprüche, worin eine oder mehrere der Monomer-, Polymerisationsinitiator- und Neutralisationsmittelströme in Form einer Lösung vorliegen.  
40
12. Verfahren nach einem der vorhergehenden Ansprüche, worin eine wäßrige Lösung eines Gemischs der Dicarbonsäure, Monocarbonsäure und Monomeren, die frei von Carboxylgruppen sind, zu dem Reaktor zugegeben wird.  
45
13. Verfahren nach einem der vorhergehenden Ansprüche, worin der Polymerisations-pH-Wert im Bereich von 4 bis 6 durch die Zugabe von 20 bis 80 Äquivalentprozent von Base, basierend auf dem Säuregehalt der Monomere, aufrechterhalten wird.
- 50 14. Verfahren nach einem der vorhergehenden Ansprüche, worin die Monomeren verschiedene Reaktionsgeschwindigkeit aufweisen, und das Produkt aus Schritt (d) restliches unreagiertes langsamer reagierendes Monomer enthält, und worin die Menge von derartigem unreagiertem langsamer reagierendem Monomer reduziert wird, indem man, anschließend an Schritt (d), einen oder mehrere der folgenden zusätzlichen Schritte durchführt:  
55
  - (a) Zugeben weiterer schneller reagierender Monomeren;
  - (b) Zugeben weiteren Initiators; und
  - (c) Erhöhen der Polymerisationstemperatur.

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15. Verfahren zur Herstellung wasserlöslicher Copolymere, umfassend Herstellen eines Anfangsreakteureinsatzmaterials von Wasser, allmähliches Dazugeben von, unter im wesentlichen einheitlichen Zugabegeschwindigkeiten, Monomeren, Polymerisationsinitiatoren und Neutralisationsmittel, als getrennte Ströme oder Gemische davon, wobei die Monomeren, Initiatoren und Neutralisationsmittel co-zugeführt werden, und die Monomeren umfassen von 3 bis 65 Gew.-%, beispielsweise 5 bis 65 Gew.-%, basierend auf der gesamten Menge der Monomeren, von mindestens einer monoethylenisch ungesättigten Dicarbonsäure mit von 4 bis 6 Kohlenstoffatomen pro Monomermolekül, ihre Salze und die Anhydride von derartigen Dicarbonsäuren, und von 35 bis 97 Gew.-%, beispielsweise 35 bis 95 Gew.-%, basierend auf der gesamten Menge der Monomeren, von mindestens einem Comonomer, ausgewählt aus monoethylenisch ungesättigten Monocarbonsäuren mit von 3 bis 6 Kohlenstoffatomen pro Monomermolekül und ungesättigten Monomeren, die frei von Carboxylgruppen sind, und Durchführen der Reaktion in Gegenwart eines Metallsalzaktivators bei von etwa 80 bis 200 °C, und sobald die Polymerisation vervollständigt ist, Gewinnen des Copolymers.
16. Detergentzusammensetzung, umfassend eine wasserlösliche Detergentverbindung, ausgewählt aus anionischen, nichtionischen, zwitterionischen, ampholytischen Detergentverbindungen und Gemischen davon, einen Builder, ausgewählt aus den Alkalimetallsalzen von Carboxymethyloxysuccinsäure und Oxydiessigsäure, Tetranatrium- und Tetrakaliumpyrophosphat, Pentanatrium- und Pentakaliumtripolyphosphaten, Etherpolycarboxylaten, Zitraten, Stärke oder Zellulose, die von Polycarboxylaten abgeleitet ist, und Polyacrylsäuren, und bis zu etwa 35 Gew.-%, beispielsweise von 0,1 bis 20 Gew.-% und vorzugsweise von 0,5 bis 5,0 Gew.-% eines Copolymers, das nach dem Verfahren nach einem der Ansprüche 1 bis 15 hergestellt ist.

## Revendications

1. Procédé de préparation de copolymères solubles dans l'eau qui comprend:
- (a) l'établissement d'une charge initiale d'eau dans un réacteur;
  - (b) l'addition progressive de monomères, d'initiateur de polymérisation et de neutralisant, qui sont ajoutés sous forme de courants séparés, ou des mélanges de ceux-ci, au réacteur, chaque courant étant ajouté à une vitesse d'addition sensiblement uniforme et les courants étant au moins initialement co-alimentés, la période de co-alimentation étant d'au moins 25%, par exemple un tiers ou plus, de la période totale d'addition des courants, et dans laquelle les monomères renferment (A) de 3 à 65% en poids, par exemple 5 à 65% en poids par rapport au poids total des monomères, d'au moins un acide dicarboxylique à insaturation monoéthylénique contenant 4 à 6 atomes de carbone par molécule de monomère, ou un de ses sels ou anhydrides, et (B) de 35 à 97% en poids, par exemple 35 à 95% en poids par rapport au poids total des monomères, d'au moins un comonomère choisi parmi les acides monocarboxyliques à insaturation monoéthylénique contenant 3 à 6 atomes de carbone par molécule de monomère et des monomères insaturés dépourvus de groupe carboxyle;
  - (c) l'addition d'un activateur à base de sel de métaux au réacteur, dans laquelle l'activateur à base de sel de métaux peut être contenu dans la charge d'eau initiale, ajouté au cours de l'addition des monomères, ajouté après l'addition d'un ou de plusieurs monomères, ou une combinaison de ceux-ci;
  - (d) la conduite de la réaction à une température allant d'environ 80 à 200 °C; et
  - (e) la récupération du copolymère résultant à partir du réacteur.
2. Procédé selon la revendication 1, dans lequel, les monomères sont ajoutés sous forme de courants de monomère séparés et l'addition est telle que les monomères sont au moins initialement co-alimentés et que la période d'une telle co-alimentation représente au moins 25% de la période totale d'addition de monomères.
3. Procédé selon la revendication 1 ou 2, dans lequel l'activateur à base de sel de métaux est choisi parmi les sels de cobalt, fer, cuivre, nickel, manganèse, zirconium et zinc, et est présent en une quantité allant de 1 à 200 ppm, par rapport au poids total des monomères.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel la concentration en acide dicarboxylique est de 10 à 60% en poids, par rapport au poids total des monomères.

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5. Procédé selon l'une quelconque des revendications précédentes, dans lequel, l'acide dicarboxylique est choisi parmi l'acide maléique, l'acide itaconique, l'acide mésaconique, l'acide fumarique, l'acide citraconique, leurs sels, leurs anhydrides, et les combinaisons de ces substances.
- 5 6. Procédé selon l'une quelconque des revendications précédentes, dans lequel, la concentration de l'initiateur est de 0,5 à 20% en poids, de préférence de 1 à 10% en poids, par rapport au poids des monomères, et/ou dans lequel, l'initiateur est choisi parmi le peroxyde d'hydrogène, le t-butyl hydroperoxyde, le persulfate de sodium, le persulfate de potassium, le persulfate d'ammonium, le perphosphate de sodium, le perphosphate d'ammonium, le perphosphate de potassium, et le 2,2-azo-bi(acide cyanovalérique).
- 10 7. Procédé selon l'une quelconque des revendications précédentes, dans lequel, une combinaison de deux ou plusieurs initiateurs est utilisée.
- 15 8. Procédé selon l'une quelconque des revendications précédentes, dans lequel, la polymérisation est menée selon une proportion en solides allant de 20 à 80%, par exemple allant de 30 à 65% en poids.
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel, le monomère monocarboxylique est choisi parmi l'acide acrylique, l'acide méthacrylique, l'acide vinylacétique, l'acide crotonique et l'acide acryloxypropionique.
- 20 10. Procédé selon l'une quelconque des revendications précédentes, dans lequel, le monomère dépourvu de groupe carboxyle est choisi parmi: les esters alkyls des acides acryliques et méthacryliques tels que l'acrylate de méthyle, l'acrylate d'éthyle, l'acrylate de butyle, le méthacrylate de méthyle, le méthacrylate d'éthyle, le méthacrylate de butyle et le méthacrylate d'isobutyle, les esters hydroxyalkyliques des acides acryliques et méthacryliques tels que l'acrylate d'hydroxyéthyle, l'acrylate d'hydroxypropyle, le méthacrylate d'hydroxyéthyle, le méthacrylate d'hydroxypropyle; l'acrylamide; le méthacrylamide; le N-tert-butyl acrylamide; le N-méthyl acrylamide; le N,N-diméthyl acrylamide; l'acrylonitrile; le méthacrylonitrile; l'alcool allylique; l'acide sulfonique allylique; l'acide phosphonique allylique; l'acide vinylphosphonique; l'acrylate de diméthylaminoéthyle; le méthacrylate de diméthylaminoéthyle; le méthacrylate de phophoéthyle; la N-vinyl pyrrolidone; le N-vinylformamide; le N-vinylimidazole; le diacrylate d'éthylène glycol; le triacrylate de triméthylolpropane; le phtalate diallylique; l'acétate de vinyle; le styrène; l'acide vinylsulfonique et les sels de celui-ci; et l'acide 2-acrylamido-2-méthylpropane sulfonique et les sels de celui-ci.
- 35 11. Procédé selon l'une quelconque des revendications précédentes, dans lequel, un ou plusieurs des courants de monomères, d'initiateur de polymérisation et de neutralisant sont sous la forme d'une solution.
- 40 12. Procédé selon l'une quelconque des revendications précédentes, dans lequel, une solution aqueuse d'un mélange de l'acide dicarboxylique, de l'acide monocarboxylique et des monomères dépourvus de groupe carboxyle est ajoutée au réacteur.
- 45 13. Procédé selon l'une quelconque des revendications précédentes, dans lequel, le pH de polymérisation est maintenu dans la gamme allant de 4 à 6 par l'addition de 20 à 80% d'équivalent de base, par rapport à la teneur en acide des monomères.
- 50 14. Procédé selon l'une quelconque des revendications précédentes, dans lequel, les monomères ont des vitesses de réaction différentes et le produit issu de l'étape (d) contient des monomères résiduels à réaction plus lente, qui n'ont pas réagi, et dans lequel le niveau de tels monomères à réaction plus lente, qui n'ont pas réagi, est réduit par l'étape (d) suivi de la réalisation de l'une ou plusieurs des étapes supplémentaires suivantes:
  - (a) addition de monomère supplémentaire réagissant plus rapidement;
  - (b) addition d'initiateur supplémentaire; et
  - 55 (c) élévation de la température de polymérisation.
15. Procédé de préparation de copolymères solubles dans l'eau qui comprend l'établissement d'une charge initiale d'eau du réacteur, l'addition progressive, à des vitesses d'addition sensiblement

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uniformes, de monomères, d'initiateurs de polymérisation et de neutralisant, au réacteur, sous forme de courants séparés, ou des mélanges de ceux-ci, les dits monomères, initiateurs et neutralisant étant co-alimentés et lesdits monomères comprenant 3 à 65% en poids, par exemple 5 à 65% en poids par rapport à la quantité totale de monomères, d'au moins un acide dicarboxylique à insaturation monoéthylénique contenant 4 à 6 atomes de carbone par molécule de monomère, leurs sels et les anhydrides de tels acides dicarboxyliques, et 35 à 97% en poids, par exemple 35 à 95% en poids par rapport à la quantité totale de monomères, d'au moins un comonomère choisi parmi les acides monocarboxyliques à insaturation monoéthylénique contenant 3 à 6 atomes de carbone par molécule de monomère et des monomères insaturés dépourvus de groupe carboxyle, et la conduite de ladite réaction en présence d'un activateur à base de sel de métaux, à une température allant d'environ 80 à 200 ° C, et une fois la polymérisation terminée, la récupération du dit copolymère.

16. Composition détergente qui comprend un composé détergent soluble dans l'eau choisi parmi des composés détergents anioniques, non ioniques, zwitterioniques, ampholytiques, et les mélanges de ces composés; un adjuvant choisi parmi les sels de métaux alcalins d'acide carboxyméthoxyloxysuccinique et d'acide oxydiacétique, de pyrophosphate de tétrasodium et de tétrapotassium, de tripolyphosphates de pentapotassium et de pentasodium, de polycarboxylates d'éther, de citrates, d'amidon ou de cellulose dérivés de polycarboxylates, et d'acides polyacryliques, et jusqu'à environ 35% en poids, par exemple 0,1 à 20% en poids, et de préférence 0,5 à 5,0% en poids, d'un copolymère préparé selon le procédé de l'une quelconque des revendications 1 à 15.

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Figure I

